Sp 2004 Final Organic II

200pts (Weighted as 300)

Name

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Good luck and please read the questions!

1) Identify the class of compounds each of the following molecules belong to (22.5pts).

2) Circle the molecule that would be most basic. (1.5pts)

3) Put crosses through the two compounds which have a triple bond. (3pts)
4) Identify each of the below reactions as an *addition*, *condensation*, *elimination* or *substitution*. (16pts)

(a)  \[
\begin{align*}
\text{O} & \quad \text{CH}_2\text{OH} \\
\text{PCC} & \quad \rightarrow \\
& \quad \text{CHO}
\end{align*}
\]

(b)  \[
\begin{align*}
\text{O} & \quad \text{R} \quad \text{R} \\
\text{NaBH}_4 & \quad \rightarrow \\
& \quad \text{R} \quad \text{OH} \quad \text{R} \quad \text{H}
\end{align*}
\]

(c)  \[
\begin{align*}
\text{CF}_3 & \quad \text{C} \quad \text{C} \quad \text{CF}_3 \\
\text{O} & \quad \text{R} \quad \text{RR} \\
\rightarrow & \quad \text{CF}_3 \quad \text{CF}_3 \quad \text{CF}_3 \quad \text{CF}_3
\end{align*}
\]

(d)  \[
\begin{align*}
\text{R} & \quad \text{O} \quad \text{Cl} \\
\text{OH} & \quad \rightarrow \\
& \quad \text{R} \quad \text{OH}
\end{align*}
\]

(e)  \[
\begin{align*}
\text{OH} & \quad \rightarrow \\
& \quad \text{R} \quad \text{N} \quad \text{O}_2
\end{align*}
\]

(f)  \[
\begin{align*}
\text{O} & \quad \text{R} \quad \text{R} \\
\text{H}_2\text{O} & \quad \rightarrow \\
& \quad \text{R} \quad \text{OH} \quad \text{R} \quad \text{OH}
\end{align*}
\]

(g)  \[
\begin{align*}
\text{CH}_3\text{O}^- & \quad \rightarrow \\
& \quad \text{R} \quad \text{F} \quad \text{O} \quad \text{CH}_3
\end{align*}
\]

(h)  \[
\begin{align*}
\text{O} & \quad \text{R} \quad \text{R} \\
\text{HS-CH}_2\text{CH}_2\text{-SH} & \quad \rightarrow \\
& \quad \text{R} \quad \text{S} \quad \text{S} \quad \text{R} \quad \text{R}
\end{align*}
\]
5) The following reactions are named after their inventors - give the names of the following reactions (10.5pts).

(a) \[
\text{ benzene } \rightarrow \text{ benzene } \text{CH}_2\text{CH}_2\text{CH}_3
\]

(b) \[
\text{ benzene } \rightarrow \text{ benzene }
\]

(c) \[
\text{ [Diagram of reaction] } \rightarrow \text{ [Diagram of product] }
\]

(d) \[
\text{ [Diagram of reaction] } \rightarrow \text{ [Diagram of product] }
\]

(e) \[
\text{ [Diagram of reaction] } \rightarrow \text{ [Diagram of product] }
\]

(f) \[
\text{ [Diagram of reaction] } \rightarrow \text{ [Diagram of product] }
\]

(g) \[
\text{ [Diagram of reaction] } \rightarrow \text{ [Diagram of product] }
\]
6) Give an *advantage* and a *disadvantage* of Molecular orbital theory. (4pts).

7) State whether each of the following Molecular orbitals are overall bonding, antibonding or non bonding (4.5pts)

(a) 

(b) 

(c) 

8) Draw two Lewis resonance structures for a carboxylate anion $\text{RCO}_2^-$ (4pts)

9) Draw also the corresponding resonance hybrid structure (2pts).
10) Indicate which of the following molecules are aromatic, non-aromatic or anti-aromatic. (Assume all the molecules are planar). (15pts)

11) Explain why BENZYNE, shown below, is correctly described as a 6\pi aromatic compound. (8pts)
12) Give the products in **six** of the following reactions, paying attention to regio/stereochemistry where applicable. (18pts)

- \[
\text{Cyclopentadiene} + \text{NC} \equiv \text{CN} \xrightarrow{\text{heat}} \text{products}
\]
- \[
\text{PhOH} \xrightarrow{1) \text{NaOH}} \xrightarrow{2) \text{CH}_3\text{CH}_2\text{I}} \text{products}
\]
- \[
\text{PhCH} = \text{CHPh} \xrightarrow{\text{Br}_2, \text{H}_2\text{O}} \text{A} \xrightarrow{\text{KOH}} \text{B}
\]
- \[
\text{O-CH}_2\text{CH}_2\text{O} \xrightarrow{\text{Excess HI}} \text{products}
\]
- \[
\text{PhCH}_3 \xrightarrow{\text{CO, HCl, CuCl, AlCl}_3} \text{products}
\]
- \[
\text{PhNO}_2 \xrightarrow{1) \text{Zn, HCl}} \xrightarrow{2) \text{NaNO}_2, \text{HCl}} \xrightarrow{3) \text{CuCl, HCl}} \text{products}
\]
- \[
\text{PhCH}_3\text{NHCOCH}_3 \xrightarrow{\text{Br}_2, \text{FeBr}_3} \text{products}
\]
13) For both below substitution reactions:
   (i) draw the expected product
   (ii) explain why the bromine substitutes at that specific site for each reaction. (13pts)

\[ \text{CH}_3 \text{Br}_2, \text{FeBr}_3 \text{Br}_2, \text{uv light} \]

\[ \text{O}_2\text{N} \]

\[ \text{CH}_3 \]

\[ \text{Br}_2, \text{FeBr}_3 \]
14) Give reagents and conditions to accomplish five of the following transformations. (15pts)
15) Circle the stronger base in the following pairs. (10pts)

(a)  
(b)  
(c)  
(d)  
(e)  

16) Circle the stronger acid in the following pairs. (8pts)

(a)  
(b)  
(c)  
(d)  

17) Name **five** of the following compounds in IUPAC form (14pts).

![Compounds](image)

18) The following compound was produced in a (4+2) cycloaddition.

![Diene and Dienophile](image)

How many carbons are in the molecule? (2pts)

Draw the diene and dienophile which react together to give this product. (4pts)
19) Fill in the blanks. (9pts)
20) Give the mechanism for **two** of the below conversions (16pts)

(a) \[
\begin{align*}
\text{NH}_2 & \quad \text{1) excess CH}_3\text{Br} \\
\end{align*}
\]
\[
\begin{align*}
\text{NH}_2 & \quad \text{2) Ag}_2\text{O, H}_2\text{O, heat} \\
\end{align*}
\]

(b) \[
\begin{align*}
\text{C}_6\text{H}_5 & \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} \\
\text{AlCl}_3 & \quad \rightarrow \\
\end{align*}
\]

(c) \[
\begin{align*}
\text{Ph} & \quad \text{CH}_3\text{CH}_2\text{NH}_2 \\
\text{H}_2\text{SO}_4 & \quad \rightarrow \\
\text{Ph} & \quad \text{Ph} \\
\end{align*}
\]
*Bonus question* (up to 5 points)

*Either* draw a sketch of someone in this room

*Or*

List 5 (serious) ways the organic lecture and/or lab experience could be improved.
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Good luck and please read the questions!

1) Identify the class of compounds each of the following molecules belong to (22.5pts).

2) Circle the molecule that would be most basic. (1.5pts)

3) Put crosses through the two compounds which have a triple bond. (3pts)
4) Identify each of the below reactions as an addition, condensation, elimination or substitution. (16pts)

(a) $\text{CH}_2\text{OH} \xrightarrow{\text{PCC}} \text{CHO} \quad \text{Eum}$

(b) $\text{R}\text{C}=\text{C}\text{R} \xrightarrow{\text{NaBH}_4} \text{R}\text{OH} \quad \text{Add}$

(c) $\text{CF}_3\text{C}=\text{C}\text{CF}_3 \xrightarrow{\text{HC}} \text{CF}_3\text{CF}_3 \quad \text{Add}$

(d) $\text{R}\text{C}=\text{C}\text{O} \xrightarrow{\text{OH}} \text{R}\text{COOH} \quad \text{Subst}$

(e) $\text{CH}_2=\text{CH}_2 \xrightarrow{\text{HNO}_3} \text{CH}_2=\text{CH}_2\text{NO}_2 \quad \text{Subst}$

(f) $\text{R}\text{C}=\text{C}\text{R} \xrightarrow{\text{H}_2\text{O}} \text{R}\text{OH} \quad \text{Add}$

(g) $\text{CF}_3\text{C}=\text{C}\text{CF}_3 \xrightarrow{\text{CH}_3\text{O}^-} \text{CF}_3\text{C}=\text{C}\text{CF}_3 \quad \text{Subst}$

(h) $\text{R}\text{C}=\text{C}\text{R} \xrightarrow{\text{HS-CH}_2\text{CH}_2=\text{SH}} \text{R}\text{S} \text{S}\text{R} \quad \text{Condensation}$
5) The following reactions are named after their inventors - give the names of the following reactions (10.5pts).

(a) \[
\text{Cyclohexane} \rightarrow \text{Benzene}
\]
\[\text{Friedel-Crafts Alkylation}\]

(b) \[
\text{Benzene} \rightarrow \text{Benzene}
\]
\[\text{Birch Reductive Cyclization}\]

(c) \[
\text{[Furan] + CF}_3\text{C} \rightarrow \text{[Furan] + CF}_3\text{C}
\]
\[\text{Dels-Alder Cycloaddition}\]

(d) \[
\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH} = \text{CH}_2
\]
\[\text{Hoffman Elimination}\]

(e) \[
\text{R} = \text{NH}_2 \rightarrow \text{R} = \text{NH}_2
\]
\[\text{Hoffman Rearrangement}\]

(f) \[
\text{RCOR} \rightarrow \text{RC} = \text{RC}
\]
\[\text{Wittig Reaction}\]

(g) \[
\text{RCOH} \rightarrow \text{RCOR}
\]
\[\text{Fischer Esterification}\]
6) Give an advantage and a disadvantage of Molecular orbital theory. (4pts).

Adv: Accurate description of π bonding
- Can explain aromaticity and anti-aromaticity
- Can explain "allowed" vs. "forbidden" cycloaddition

Dis: Complex/confusing
- Can't write easy arrow mechanisms.

7) State whether each of the following Molecular orbitals are overall bonding, antibonding or non bonding (4.5pts)

(a) [Diagram]

(b) [Diagram]

(c) [Diagram]

8) Draw two Lewis resonance structures for a carboxylate anion RCO₂⁻ (4pts)

\[
\begin{align*}
\text{R} & \equiv \text{O}^- \\
\leftrightarrow & \\
\text{R} & \equiv \text{O}^-
\end{align*}
\]

9) Draw also the corresponding resonance hybrid structure (2pts).

\[
\begin{align*}
\text{R} & \equiv \text{O}^- \\
\end{align*}
\]
10) Indicate which of the following molecules are aromatic, non-aromatic or anti-aromatic. (Assume all the molecules are planar). (15pts)

\[
\begin{array}{cccc}
\text{Non} & \text{Non} & \text{Non} & \text{Non} \\
\text{Anti} & \text{Anti} & \text{Aromatic} & \text{Aromatic}
\end{array}
\]

11) Explain why BENZYLE, shown below, is correctly described as a 6π aromatic compound. (8pts)

There are 6π e⁻s overlapping in the same plane as the ring.

The triple bond only contributes only 2π electrons to the π system.

The 'other' π bond is incorrectly aligned which prevents overlap.
12) Give the products in **six** of the following reactions, paying attention to regio/stereochemistry where applicable. (18pts)

\[ \text{NC} \equiv \text{CN} \xrightarrow{\text{heat}} \]

\[ \text{Ph-CH}_{2} \xrightarrow{\text{Br}, \text{H}_2\text{O}} \]

\[ \text{CH}_{3} \text{O} \xrightarrow{\text{Excess HI}} \]

\[ \text{NO}_{2} \xrightarrow{1) \text{Zn, HCl}} \xrightarrow{2) \text{NaNO}_{2}, \text{HCl}} \xrightarrow{3) \text{CuCl, HCl}} \]

\[ \text{Ph-CH}_{3} \xrightarrow{\text{Br}, \text{FeBr}_{3}} \]
13) For both below substitution reactions:

(i) draw the expected product

(ii) explain why the bromine substitutes at that specific site for each reaction. (13pts)

This is free radical bromination. The uv light generates Bromine Radicals.
\[ \text{Br}_2/\text{Br} \rightarrow \text{Br} + \cdot\text{Br} \]
The radicals abstract the H with the lowest B.D.E (\(\rightarrow\) most stable carbon radical)

The benzylic H is selectively removed to yield a resonance stabilized radical.

(this reaction is Electrophilic Aromatic Substitution.
The \(\text{NO}_2\) is para-directing, the \(\text{CH}_3\) is ortho/para directing. There is steric reinforcement.)
14) Give reagents and conditions to accomplish five of the following transformations. (15pts)

\[ \text{PhCO}_2\text{H} \xrightarrow{\text{SOCl}_2} \overset{\text{LiAlH}(\text{OBu})_3}{A} \xrightarrow{\text{H}_2, \text{Ni}} \text{PhCHO} \]

\[ \text{CH}_2=\text{CHCO}_2\text{H} \xrightarrow{\text{H}_2, \text{Ni}} \text{CH}_2\text{CH}_2\text{CO}_2\text{H} \]

\[ \text{PhCH}_3 \xrightarrow{\text{Br}_2, \text{h}_2\text{O}} \overset{\text{Na}_2\text{CN}}{A} \]

\[ \text{CH}_3\text{CH}=\text{CHCH}_3 \xrightarrow{1) \text{PhMe}_2\text{Br}, 2) \text{H}_3\text{O}^+} \]

\[ \text{PhO}_2\text{NCH}_2\text{CN} \xrightarrow{1) \text{PhMe}_2\text{Br}, 2) \text{H}_3\text{O}^+} \]

\[ \text{PhCH}=\text{CHCO}_2\text{CH}_3 \xrightarrow{\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}, \text{H}^+} \]
15) Circle the stronger base in the following pairs. (10pts)

(a) \( \text{HN} = \text{CH}_3 \) \( \text{NH}_2 \)
(b) \( \text{CH}_3\text{-NH}_2 \) \( \text{NH}_3 \)
(c) \( \text{pyridine} \) \( \text{benzene} \)
(d) \( \text{H}_2\text{C} = \text{NH} \) \( \text{CH}_3 \)
(e) \( \text{NH}_3 \) \( \text{H}_2\text{O} \)

16) Circle the stronger acid in the following pairs. (8pts)

(a) \( \text{H}_3\text{C} - \text{C} - \text{OH} \) \( \text{CH}_3\text{CH}_2 - \text{OH} \)
(b) \( \text{CO}_2\text{H} \) \( \text{NO}_2\text{-phenyl} \)
(c) \( \text{Cl}_3\text{C} - \text{C} - \text{OH} \) \( \text{Br}_3\text{C} - \text{C} - \text{OH} \)
(d) \( \text{F}_{\text{tetrafluorocyclohexy}l} \text{CO}_2\text{H} \) \( \text{F}_{\text{cyclohexyl}} \text{CO}_2\text{H} \)
17) Name **five** of the following compounds in IUPAC form (14pts).

- 4-Fluoro-(3,2)butenal
- Propanoic Ethanoic Anhydride
- Butanoyl Bromide
- 5-Hydroxy pentanoic acid lactone
- 5-amino-(2,6)hexanoic acid
- N-ethyl N-methyl propanamide

18) The following compound was produced in a (4+2) cycloaddition.

![Cycloaddition Product](image)

How many carbons are in the molecule? (2pts) **8**

Draw the diene and dienophile which react together to give this product. (4pts)
19) Fill in the blanks. (9pts)

\[
\begin{align*}
\text{HO}_2\text{ZnCl}_2, \text{H}^+ \quad & \quad \text{HO}_2\text{ZnCl}_2, \text{H}^+ \\
\text{NaOH} \quad & \quad \text{KMnO}_4 \\
\text{H}_2\text{O}^+ \quad & \quad \text{H}_2\text{O}^+ \\
\text{CH}_3\text{NH}_2 \quad & \quad \text{CH}_3\text{NH}_2 \\
\text{H}^+ \quad & \quad \text{H}^+
\end{align*}
\]
20) Give the mechanism for two of the below conversions (16pts)

(a) \[
\begin{align*}
\text{cyclohexylamine} & \xrightarrow{1) \text{excess CH}_3\text{Br}} \text{cyclohexane} \\
& \xrightarrow{2) \text{Ag}_2\text{O, H}_2\text{O, heat}} \\
\end{align*}
\]

(b) \[
\begin{align*}
\text{benzene} & \xrightarrow{\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}} \text{benzyl chloride} \\
& \xrightarrow{\text{AlCl}_3} \text{benzyl chloride} \\
\end{align*}
\]

(c) \[
\begin{align*}
\text{benzophenone} & \xrightarrow{\text{CH}_3\text{CH}_2\text{NH}_2, \text{H}_2\text{SO}_4} \text{2-phenylacetamide} \\
\end{align*}
\]